

THE SEA

VOLUME 5: Marine Chemistry

Edited by EDWARD D. GOLDBERG



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**Ideas and Observations on Progress in the Study
of the Seas**

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23. ORIGIN OF THE OCEAN

GUSTAF ARRHENIUS, BIBHAS R. DE, AND HANNES ALFVÉN

1. Sources of New Information

Our records of the early history of the ocean and of the composition and evolution of the interior of our planet are fragmentary. Inquiries based on modern geophysical and geochemical data were made in the classical studies by Rubey (1951, 1955) and Urey (1952) and in other important papers related to this subject and referred to in context below.

Lars Gunnar Sillén's interest was drawn to the early phase of the Earth's history as a logical extension of his fundamental work on the chemical dynamics of the ocean. The question of how the controlling chemical processes differed from now at the time when life was possibly absent was one of the last scientific problems that he embarked on (Sillén, 1965, 1966). He also began to devote his interest to the primordial condensation processes in space, using thermodynamic equilibrium considerations as a first, although admittedly unrealistic, approximation. The usefulness of such an approach in guiding necessary disequilibrium considerations (Arrhenius, 1972; Arrhenius and Alfvén, 1971) has subsequently been demonstrated by Lord (1965), Larimer (1967), Anders (1971), and most recently by Grossman (1972).

In the last 5 yr, experimental data have been obtained which are of great significance in shaping our ideas about the origin and evolution of the Earth's ocean and atmosphere. New insights have been gained from theoretical developments inspired largely by the exploration of space. Among materials that cast new light on the early history of the planet are the oldest known preserved sedimentary rocks from South Africa (~ 3.0 Gy; Engel et al., 1968) and preserved crustal sections as old as 3.9 Gy recently found in Greenland (Black et al., 1971). The intensified studies of meteorites have also given important clues to the sources of the Earth's atmosphere and ocean. (Wasson, 1969; Fanale, 1971). Most importantly, the exploration of the Moon has placed the planetary evolution and the history of the Earth in an entirely new perspective. This is being further broadened by missions to still more primitive objects in the solar system: comets, asteroids, and planetary satellites.

The new facts accumulating from measurements on the lunar surface and on samples returned from the Moon are providing perhaps the most important guidance in assessment of the various possibilities for the evolution of the Earth. These observations have drawn attention to circumstances of crucial importance in the early history of the planet that now appear straightforward but that were nonetheless largely ignored in the Earth-limited era of earth sciences. In general, these results emphasize the fact that the problems of the origin and evolution of the ocean and the atmosphere cannot be resolved realistically without referring to the processes by which the Earth itself

formed. The observational data pertinent to these problems do not support the previously common notion that the differentiation took place and the ocean and the atmosphere developed only after the Earth had already formed. On the contrary, the processes leading to the formation of the Earth must themselves play a decisive role in producing the differentiation and in giving rise to the precursors for the present ocean and atmosphere while the Earth was still in a state of formation.

2. Formation of the Solar System

It is now generally believed that the creation of planets can only take place by accumulation of small solid bodies (planetesimal accretion). Formation of planets from individual contracting gas clouds is excluded because of insufficient gravitation; such a process seems impossible even for a giant planet such as Jupiter (Hattori et al., 1969; Kumar, 1972). Hence, it is likely that the Earth has accumulated from a large number of small bodies in space. Considerations of orbital and spin characteristics of the Earth and other planets and their satellites place stringent requirements or limitations on the assumed dynamic state of these building blocks referred to here as grains, aggregates, embryos, and planetesimals (Alfvén, 1942 to 1945; Schmidt, 1944; Safronov, 1954; Alfvén, 1954; Levin, 1972; Alfvén and Arrhenius, 1970a, 1973).

When the formation of our solar system began, matter in the form of gas and dust must somehow have become emplaced in the circumsolar region. Several different explanations of this emplacement have been suggested; reviews of these are given by ter Haar (1967) and Hartmann (1972). Most theories attempt an explanation of the present properties of the planetary system but ignore the three well-developed satellite systems.

In an evolutionary scheme that attempts to account for the present state of both planetary and satellite systems (Alfvén and Arrhenius, 1970a, b, 1973), the Sun at the outset attracted gas and dust by gravitation. The history of formation of the Sun itself is highly uncertain; it could have been formed by collapse of a gas cloud, but equally well could have been formed by a stellesimal accretion process similar to the planetesimal process. None of these processes have been observationally verified. In contrast, the processes that can realistically be invoked to explain the late evolution of the solar system and, with less certainty, the formative state, can all be identified with processes observable today.

The neutral gas particles in the circumsolar region presumably became ionized upon reaching their critical velocity for ionization by gravitational acceleration toward the Sun. The same process occurred around the magnetized protoplanets (Jupiter, Saturn, and Uranus) after their formation. The resulting plasma was stopped by the magnetic field at various distances from these central bodies, determined by the atomic mass and the ionization potential of the controlling chemical species in the neutral gas. The plasma was brought into its necessary rotational state by magnetohydrodynamic transfer of angular momentum from the central bodies.

Under the combined action of the gravitational and the magnetic fields, the plasma acquired a state of motion referred to as partial corotation. The plasma rotating around the Sun provided the material that, after condensation to small particles, aggregated to larger bodies that ultimately gave rise to the planets. The theory draws on the similarity between the planetary system and the three regular satellite systems (Jovian, Saturnian, and Uranian) and stresses that the regular satellites must have formed around the planets by the same series of processes by which the planets formed around the Sun. The existence of four analogous systems thus removes the constraint of relying solely on the Sun-planet system for relevant information.

3. Occlusion of Volatiles in Solid Condensates

Condensation from the partially corotating plasma around the Sun led to the formation of solid grains, which, by inheriting the momentum of the parent plasma, assumed eccentric Kepler orbits. Such grains appear to have been preserved to this day in space as aggregates; some fragments of these are dense and strong enough to survive passage through the atmosphere and are known to us as meteorites.

Individual grains of this kind are abundant components of certain types of meteorites (carbonaceous chondrites). Such grains often form isolated crystals and twins of high regularity (Fig. 1) or rounded crystalline aggregates with cavities preserving the crystal-vapor interface and showing delicate growth features such as freely grown calcium silicate fibers (Fuchs, 1969).

This meteoritic material, believed to represent a primordial condensate but not necessarily to be identified with the material that formed the Earth, also has chemical features indicative of the conditions of growth. Among these is the incorporation of volatile components such as noble gas atoms and halogen and hydroxyl ions in some types of crystals. The noble gas components are particularly useful for the study of the mode of incorporation, since they do not develop strong chemical bonds with the host structure.

Aside from surface implanted and radiogenic components, which have different and characteristic signatures and will not be discussed here, the noble gas component of particular interest to the problems of the Earth is the component that is strongly bound through the volume of the crystals and requires high-activation energies for release. This indicates that the noble gas atoms were incorporated as impurities in crystal imperfections at growth from the vapor phase.

The fact that the occluded noble gas component is strongly bound internally in the crystals shows that the incorporation took place as a part of the crystallization process and not by subsequent surface adsorption or other low-energy processes. Furthermore, it is well known from experiments that for such noble gas occlusion to be significant, the temperature of the crystals has to be below the range 400 to 600°K. The vapor phase temperature, however, must have been an order of magnitude higher for several reasons. One such reason is the requirement for sufficient concentration of vapor components to permit growth; at the low vapor pressures of silicates and oxides, this is not possible if the vapor were in temperature equilibrium with the grains at the temperature indicated (Arrhenius and Alfvén, 1971). Another reason is the need for the gas particles to provide sufficient kinetic energy to heat the grains at the relevant plasma densities ($\lesssim 10^{12}/\text{cm}^3$). These maximum densities are required to permit the momentum transfer process to operate. In this density range, gas temperatures of the order 10^4 °K are required (Lehnert, 1970; Arrhenius, 1972; De and Arrhenius, 1973) to maintain grain temperatures in the range of 300 to 900°K indicated by the chemical record (Larimer, 1967; Larimer and Anders, 1967, 1970; Grossman, 1972).

Hence we are concerned with a thermal steady state that must be common in gas-solid systems in space and where crystallizing grains at comparatively low temperature are immersed in, and exchange matter and energy with, a hot, optically thin, partially ionized gas.

4. Primordial Grains as Carriers of Atmospheric and Oceanic Components

The composition of the occluded noble gas component in primordial condensates gives useful clues to the origin of the atmosphere of the Earth and the formation of its ocean. Measurements on meteorites show that this component characteristically

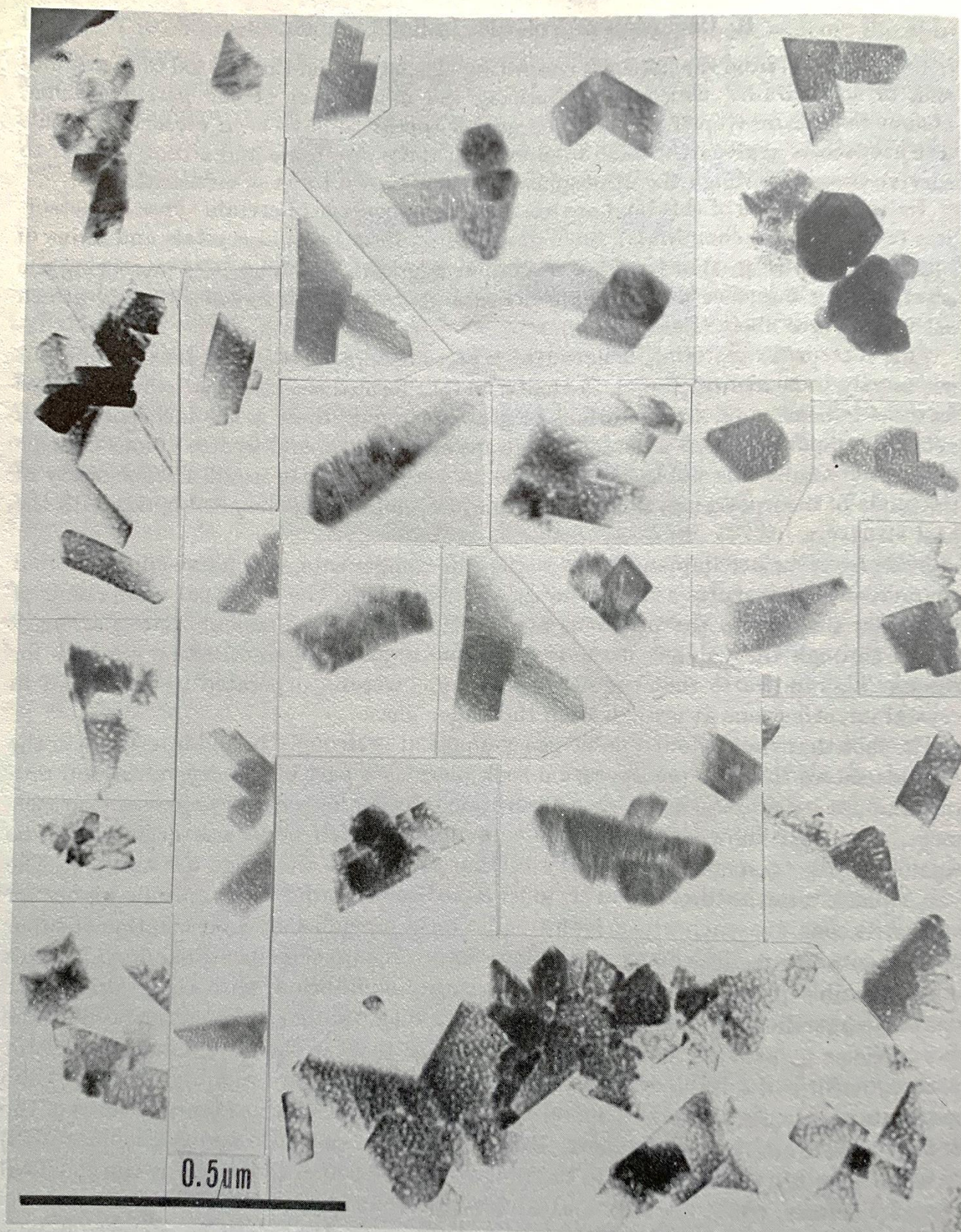


Fig. 1. Delicate, leafy crystals of the magnesium-iron silicates of olivine and pyroxene, frequently twinned, and loosely adhering to each other. These crystals form a characteristic component of the porous regions of the carbonaceous chondrite Allende. The thickness of the crystal leaves is of the order of $100 \text{ \AA}$, tapering off toward the edges. The crystal habit and the lack of significant adhesion show that the crystals and twinned aggregates grew from a vapor phase. The preservation of their delicate features indicates their relative velocities at aggregation must have been low, perhaps in the range of meters per second or lower. From Arrhenius and Asunmaa (1973).

has a relative abundance distribution of primordial noble gas species that is closely similar to that of the Earth's atmosphere (Signer and Suess, 1963). In contrast, the solar abundances more or less accurately represented by solar wind, and by the components implanted in the surface skin of lunar rocks and meteorite grains were realized to be markedly different with a much higher abundance of light noble gases.

These facts suggest that the special noble gas composition, as found in meteorites and in the terrestrial atmosphere, was established in the gas phase from which the primordial condensates grew, both in the region of space where the parent materials of meteorites formed, and in the region where the parent material of the Earth condensed. Several mechanisms may have contributed to the observed noble gas fractionation in the circumsolar region (see reviews in Arrhenius, 1972; Black, 1972a, b).

The Earth could then have acquired its atmosphere and ocean as it grew from primordial grains and aggregates similar to, but not necessarily identifiable with those found in meteorites, by the release of the volatiles mainly during the accretion process into a primordial atmosphere from which the present one has gradually developed (Aston, 1924).

Although the important discovery of the "planetary" component of noble gases in meteorites was made over a decade ago, the full implications of a genetic relationship was not realized until recently (Wasson, 1969; Fanale, 1971). Fanale aptly ascribes this delay to a climate of opinion that for a long time fostered a belief that the primordial atmosphere of the Earth must have been entirely removed by some *ad hoc* process. The present atmosphere would under these circumstances have evolved entirely by degassing the interior of the planet, which then would need from the outset to have retained a sufficient mass of volatile components.

As demonstrated by Fanale, this is not likely to have been the case; the primordial noble gases with the possible exception of xenon must at accretion onto Earth have been largely transferred to the atmosphere where they still reside. They do not appear to play a significant role in the present gas flux from the Earth's interior, where the noble gas component is dominated by radiogenic species, nor do they occur in measurable quantities in igneous rocks. Other chemically reactive volatiles show a more complex partition between the atmosphere and the solid Earth, as discussed below.

The component of primordial solids of major importance as a source of oceanic water is hydroxyl ion. This ion forms a regular structural element in magnesium and iron hydroxysilicates with sheet structure, which form the major mass of carbonaceous chondrites of Type I (Wiik, 1956). (Crystal hydrates of magnesium and sodium sulfates found in carbonaceous chondrites are probably not generated in space where they are unstable; they are likely to be forming by reaction with water vapor in terrestrial museums.)

It was previously believed (on the basis of geological experience) that the hydroxysilicates in meteorites must be understood as a secondary reaction product between anhydrous silicates and water in vapor form, or even as liquid water in rivers and swamps on a planet from which the sediments would subsequently have been removed as meteorites. It is now known from experiment (Meyer, 1969, 1971) that magnesium hydroxysilicates, analogous to those in meteorites, crystallize directly from partially ionized gas containing magnesium, silicon, hydrogen, and oxygen species and at grain temperatures below about 500°K. Furthermore, substitution with hydroxyl occurs also in the terrestrial varieties of silicates, common in space, such as olivine and pyroxene (Martin and Donnay, 1972). Such partial hydroxylation is likely to occur

also at the growth of these silicates in free space, particularly in vapor crystallization at high relative pressure of atomic and ionic species of oxygen and hydrogen.

In view of the small mass of the hydrosphere compared to the mantle (1/3000) concentrations as small as 300 ppm of available hydroxyl in the accreting silicates are sufficient to generate the total mass of the hydrosphere, considering also the initial loss process discussed in Section 9. Thus the space condensates that we know from meteorites fallen on the Earth and on the Moon (Gibson and Moore, 1973a; Apollo 16 PET, 1973) would provide ample sources for both the ocean and the atmosphere.

This should not be taken to mean that the Earth formed from any of these specific materials, which represent different condensation regions and events in space. But the observations imply that primordial condensates in different parts of the solar system, although varying markedly in chemical composition (Alfvén and Arrhenius, 1973, Part IV), have incorporated substantial amounts of volatiles, which were subsequently released in the accretional heat front at the formation of planets (Alfvén and Arrhenius, 1970b).

An important related question concerns the chemical composition of the Earth's total store of primordial volatiles, determined by the average composition of the planetesimals from which the Earth was built and modified by the loss processes discussed in the following material. In the case of the primordial noble gases, the observations previously mentioned indicate relative elemental and isotopic proportions similar to those found in meteorites and concentrations within the range of those in meteorites.

The content and proportion of reactive volatiles in the Earth's source material (primarily species of H, C, N, O, S, and the halogens) is obscured by the fact that the fraction of each one of these, hidden in the Earth's interior, is totally unknown. Analyses of crustal rocks and extrusions from the upper mantle are not informative on this point since they are likely to be contaminated by the ocean's atmospheric reservoir. Extraterrestrial materials do not provide much quantitative guidance on this point either, since their absolute and relative contents of reactive volatiles are extremely variable (Gibson and Moore, 1973b; Gibson and Johnson, 1971, 1972; Gibson, 1973).

5. The Immediate Precursor Stages

As shown above, we can trace the Earth's ocean and atmosphere with some certainty into the plasma phase, which preceded the formation of solid grains around the Sun. We shall now turn our attention to those stages of the protoplanetary development that have a most immediate effect on the formation of the ocean.

The first problem we must solve is that of the orbital evolution of a large number of grains born in eccentric Kepler orbits around the Sun and undergoing mutual collisions that result in loss of orbital energy. The result of analysis of this many-body problem (Alfvén, 1970; Baxter and Thompson, 1971, 1973; Trulsen, 1971) is contrary to intuitive application of experience from scattering of particles in a stationary frame of reference. If the particles are orbiting in a gravitational field, and if the collision time is long compared to the orbital period, the particle orbits, instead of spreading increasingly widely in space, contract into a torus (Fig. 2) whose thickness decreases with time until a state is reached where the collision velocity is low.

The exchange of energy at the particle collisions tends to equalize eccentricity, orbital inclination, and orbital radius for all particles in the assemblage. Particle

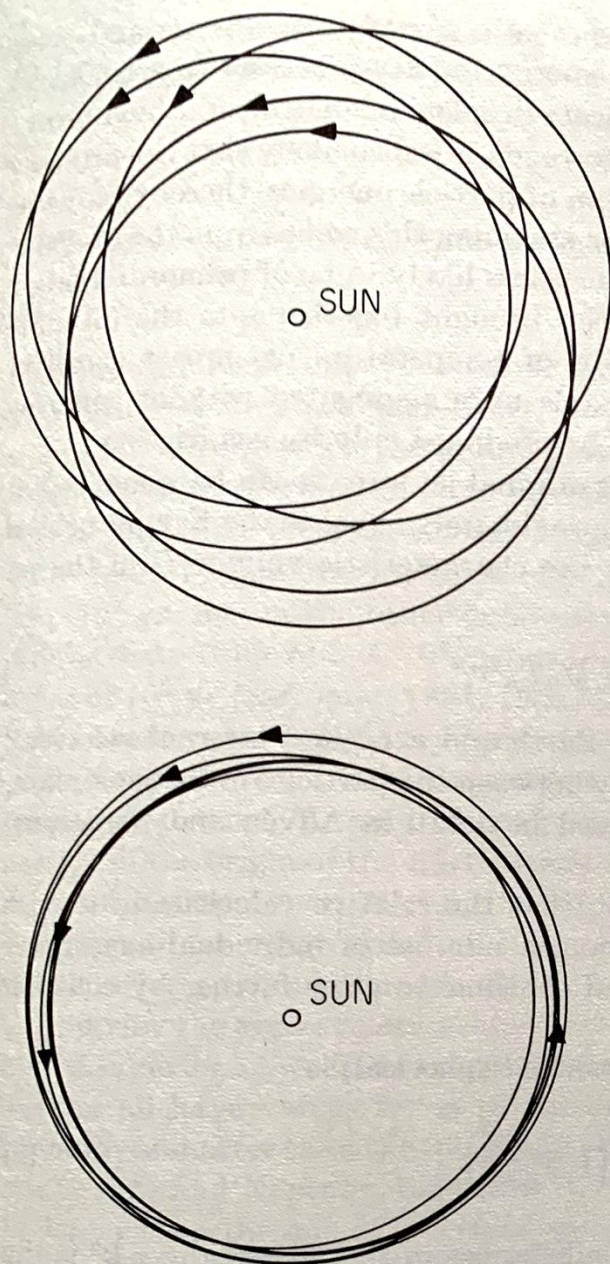


Fig. 2. The condensation process will result in a large number of small grains in eccentric Kepler orbits (top). Inelastic collisions between the grains will not spread the orbits because of the negative diffusion coefficient. Baxter and Thompson (1971, 1973). Instead the collisions will lead to equalization of the orbital elements (bottom) so that a jet stream is formed. From Alfvén and Arrhenius (1972).

assemblages with these characteristics are properly called jet streams. Such jet streams are today probably represented by groups of asteroids moving in closely similar orbits (Arnold, 1969; Danielsson, 1969, 1971). It is also possible that the particles that make up comets and meteor streams have these characteristics (Mendis, 1973).

6. Accretion of Planetary Embryos

Investigations of the lunar surface have demonstrated a number of processes leading to adhesion of colliding particles and resulting in a net growth of aggregate size (Asunmaa et al., 1970; Arrhenius and Asunmaa, 1973). This occurs when the relative velocity between the particles is low enough, or if the target is an already accreted fluffy aggregate, large enough to dissipate the projectile energy within it. Before this stage of low relative velocities in the jet stream is reached, particle collisions result in fragmentation or vaporization. Their effect is mainly a decrease of the particle size

while the resultant fragments or condensates remain parts of the stream and eventually collide again. The importance of high-energy impact processes is reflected by the large fraction of melted and quenched silicate droplets (chondrules), which form a major part of the most common meteorites. However, it is also likely that the presence of gas in jet streams leads to viscous dissipation of particle energies, thereby reducing the relative velocities at collision. The need for assuming this comes from the observation in carbonaceous chondrites of abundant crystals likely to be of primordial origin and having a fragile texture, which have been brought together into the ultimate aggregate now observed, without destruction of temperature or impact sensitive features (Fig. 1). This requires that the crystals were aggregated without suffering high-energy collisions and such an effect can be produced only by gas friction.

The approximate dimensions of the Earth's original jet stream can be visualized in the form of a torus with the large radius r_0 approximately equal to the Earth's orbital radius with the small diameter $2x$ such that the characteristic volume U of the jet stream is

$$U = 2\pi^2 r_0 x^2 = \frac{1}{2} r_0 T_K^2 v_i^2 \quad (1)$$

where T_K is the Kepler orbital period of the Earth and v_i is the "internal velocity" in the stream representing the relative velocity between the particles in the jet stream. (The results quoted in this section are derived in detail in Alfvén and Arrhenius, 1970b, Section 9).

When the condition has been reached such that the relative velocities in the jet stream are low enough to permit net accretion, a number of individual aggregates (embryos) in the stream begin to accrete, and continue to grow further by collision with individual grains and with each other.

The rate of mass increase of an embryo (assumed spherical) is

$$\frac{dM_e}{dt} = v_i \rho \pi R^2 \left(1 + \frac{v_e^2}{v_i^2} \right) \quad (2)$$

where ρ is the space density of condensable substances in the jet stream, πR^2 is the geometrical cross section of the embryo for capture of the condensable substances, and v_e is the escape velocity of the embryo, given by

$$v_e = \left(\frac{2\kappa M_e}{R} \right)^{1/2} = \left(\frac{8}{3} \pi \kappa \theta \right)^{1/2} R \quad (3)$$

θ being the density (assumed here to be uniform) of the embryo, and κ the gravitational constant. The factor in parentheses in equation 2 represents the increase in the effective capture cross section of the embryo due to gravitational attraction. The gravitational accretion becomes important when the embryo has reached a size of the order of 100 km, and the rate of accretion increases rapidly afterward.

The rapid increase in the growth rate with the size of the embryo results in a runaway accretion process (Safronov, 1954). The rate of accretion becomes catastrophically rapid at a time τ_c after the beginning of accretion when the largest embryo in the jet stream sweeps up all the other material in the jet stream to form the protoplanet. If there were an unlimited supply of particles to the jet stream, the radius of this protoplanet would theoretically become infinite in a finite time τ_a , given by

$$\tau_a = \left(\frac{3\pi}{2\kappa} \right)^{1/2} \frac{\theta^{1/2}}{\rho} = 8.4 \times 10^3 \frac{\theta^{1/2}}{\rho} \quad (4)$$

If M is the final mass of the planet, the distributed density ρ of condensables may be approximated by $\rho = M/U$, so that equation 4 may also be written as

$$\tau_a = 8.4 \times 10^3 \theta^{1/2} \frac{U}{M} \quad (5)$$

The time τ_c at which the catastrophic growth takes place may be approximated by

$$\tau_c = (2\tau_i\tau_a)^{1/2} \quad (6)$$

where the injection time τ_i is the time during which condensing grains are continuously fed to the jet stream, replenishing those removed by accretion. This represents the time span during which the grains were condensing from the plasma, and hence the total time during which gas was injected into the circumsolar region. In the part of this region where meteorites formed, measurements of formation intervals (Podosek, 1970) indicate that the injection time cannot possibly have been less than $0.15 - 0.5 \cdot 10^8$ yr. As, on the other hand, it could not possibly be of the order 10^9 yr, an intermediate value of 3×10^8 yr has been used for τ_i . Other estimates have led to the order of 10^8 yr (Safronov, 1954, 1958, 1960, 1969; Urey, 1962). As shown in Section 8, the exact value is not very important in the case of the Earth.

The order-of-magnitude consideration of the time parameter is, however, of crucial importance. As pointed out by Levin (1972), much of the confusion in the discussion of the origin of the Earth arises from ignoring the strictures that the accretion mechanism imposes on the time factor, and from the resulting *ad hoc* assumptions of accretion times many orders of magnitude shorter than the time indicated by any quantitative accumulation theory.

Applying the above relationships to the bodies in our solar system and adopting the above value for τ_i , we find essentially three types of cases. Mercury, Venus, Earth, and Jupiter all have values for τ_c of the order 10^7 yr (3.5×10^7 yr for Earth), which probably is shorter than the total time of injection of material, τ_i . At the other extreme are Uranus and Neptune, for which the values of τ_c calculated in this manner would be larger than the age of the solar system. An intermediate group is formed by the Moon, Mars, and Saturn, for which τ_c most likely is of the same order of magnitude as τ_i .

We conclude that for Uranus and Neptune, significant growth of embryos cannot have occurred while the parent jet streams were maintained at constant volume U by continuous injection of material during τ_i . Only after τ_i could a contraction of the jet stream occur, first slowly and then rapidly increasing the space density of matter and thereby accelerating the process leading up to a catastrophic accumulation. The accumulation process would consequently continue for a time substantially longer than 10^8 yr for these two planets.

In the case of the Moon, Mars, and Saturn the catastrophic termination of accretion roughly coincided with the end of injection of matter by condensation; the present uncertainty in the value of τ_i makes it impossible to state which time was the longer.

In the third case, which includes the Earth and hence is of particular interest to us, the catastrophic accumulation of the protoplanet and the exhaustion of the parent jet stream occurred very early in the process of formation of the solar system, according to equation 6, 3.5×10^7 yr after the onset of condensation in the terrestrial region of space. The mass present at that time sufficed to give rise to a protoplanet with about half the present radius (Fig. 3). During the remaining part of the time period of injection of material, assumed to last approximately 3×10^8 yr, growth was maintained at a low and steady rate, determined by the rate of injection of newly condensed material

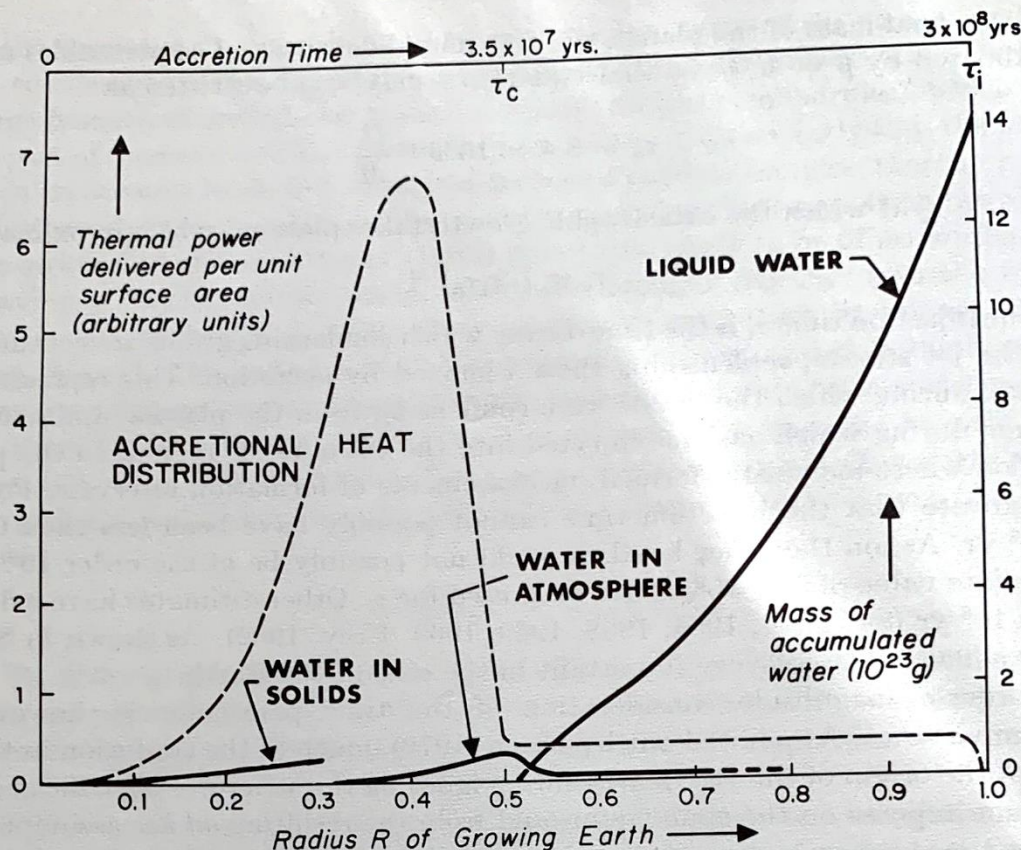


Fig. 3. The dashed curve and the left-hand ordinate scale show the thermal power (in arbitrary units) delivered per unit surface area of the growing Earth by impacting planetesimals. The lower abscissa shows the radius of the growing Earth in fractions of the present size. The upper (nonlinear) abscissa scale shows the time elapsed from inception of accretion. The three solid curves show the accumulation of water on Earth according to equation 17. The left curve represents the amount retained in the cool accreted inner core; the middle curve shows the accumulated water in the atmosphere, and the right-hand curve shows the accumulated liquid water. The final mass of accumulated water has been adjusted to equal the present ocean mass.

into the jet stream and hence by the rate of inflow of gas into this part of the circum-solar region. At the end of the injection time τ_i , the jet stream was rapidly exhausted and the accretion of the planet terminated, as shown in Fig. 3.

7. Heat Release and Volatilization of Water at Accretion

We have shown above the mass and time relationships of accretion of planets in general with special consideration of the Earth. The heating of the accreted material, carrying in it the volatile sources of the ocean and the atmosphere, is of crucial importance for fractionation of the volatiles and their ultimate disposition. The major amount of heat in the accretion process derives from the conversion of kinetic energy of the infalling bodies into thermal energy at impact.

When a grain hits an embryo, the velocity at impact is

$$v_p = (v_e^2 + v_i^2)^{1/2} \quad (7)$$

where v_e is the escape velocity for the embryo given by equation 3, and v_i is the original velocity of the grain relative to the embryo. In the later stage of accretion, v_i becomes small compared to v_e . Hence, the amount of kinetic energy released at each

impact is at least $\frac{1}{2}mv_e^2$, where m is the mass of the impacting grain. A fraction γ of this energy will be converted to thermal energy of fusion within the grain, melting a mass-fraction α of the grain, given by

$$\alpha = \frac{\gamma v_e^2}{2L} \quad (8)$$

L being the latent heat of fusion for the grain material. If we take iron-magnesium silicates to be representatives of the solid material in the grains, the latent heat of fusion (Fe_2SiO_4 : 295 J/g, MgSiO_3 : 616 J/g, Mg_2SiO_4 : 455 J/g) may be taken to be of the order of 500 J/g for our estimate. As an example, when the embryo has grown to a size of half the present size of the Earth, we find on putting $R = 0.5R_\oplus$, $\theta = 5.5 \text{ g/cm}^3$, and $L = 500 \text{ J/g}$.

$$\alpha = 25\gamma$$

Thus, even if γ is as low as 1%, one-fourth of the grain will be melted. It is likely that some of the target material will also be heated at the same time. The above is, however, a very conservative estimate, since γ is likely to be larger. Hence we can conclude that a considerable fraction of the grain will be heated to sufficiently high temperatures for the major part of its volatile components to be released in the form of gas.

The extent to which water vapor and other volatile compounds will be retained as an atmosphere around the protoplanet is determined by the balance between thermal escape of the molecules and the increasing gravitational retention by the protoplanet as its mass grows. Thus there will be a gradual accumulation of water vapor with time, and under suitable conditions this may condense to form liquid water.

These conditions are largely determined by the temperature at the surface of the growing protoplanet, which in its turn depends on the heat release at the impact of individual bodies on it as discussed above, and on the rate at which such impacts occur. Before we proceed in Section 9 to outline the process of the accumulation of water, we shall briefly review the characteristics of the accretional heat distribution.

8. Temperature Distribution in the Growing Protoplanet

The kinetic energy of an impacting planetesimal is almost directly converted to heat energy when it is brought to rest on the surface of the embryo. The thermal power w delivered per unit area of the surface of a growing embryo by the impacting planetesimals is given by

$$4\pi R^2 w = \frac{v_p^2}{2} \frac{dM_e}{dt} \quad (9)$$

Substituting equation 2 into this equation, we obtain

$$w = \frac{\rho}{8} \frac{(v_i^2 + v_e^2)^2}{v_i} \quad (10)$$

If a fraction $\gamma'w$ of this heat is dissipated in melting and vaporization of projectile and target material, then the rest $(1 - \gamma')w$, will be used up in heating the surface of the embryo. Equations 3 and 10 now give us the profile of $(1 - \gamma')w$ as a function of radius R of the growing embryo, assuming γ' to be constant. It is reasonable to assume that this heat is balanced by radiation from the surface of the embryo. Hence the profile of $(1 - \gamma')w$ will also represent the profile of the temperature of the surface

layer of the growing embryo as a function of its radius. This profile has been plotted in Fig. 3, where we note that the temperature first reaches a maximum and then falls to a very low value at the end of the time τ_c . The fraction of the mass accumulated by the time τ_c is reached is

$$\phi = \frac{\tau_c}{\tau_i} = \left(\frac{2\tau_a}{\tau_i} \right)^{1/2} \quad (11)$$

The radius of the protoplanet at this time, R_c , equals $\beta R_\oplus$, where $R_\oplus$ is the final radius, with

$$\beta = \phi^{1/3} = (2\tau_a/\tau_i)^{1/6} \quad (12)$$

Using the values 2×10^6 yr found for τ_a for the Earth, and taking $\tau_i = 3 \times 10^8$ yr, we find

$$\beta = \left(\frac{4}{300} \right)^{1/6} \approx 0.5 \quad (13)$$

The result is not very sensitive to the choice of value for τ_i ; values of 10^8 and 10^9 yr change the value for β to 0.58 and 0.40, respectively.

We conclude, therefore, that the inner core of the Earth accreted cold (Fig. 3), the accretion temperature rose to maximum at the formation of the outer core and then fell abruptly and remained low (averaged over the entire surface of the Earth) during the accretion of the mantle. It is tempting to see in this primeval heat distribution of the Earth an explanation of the fact that in its present state, our planet is known to have a solid inner core and mantle and a liquid outer core. This requires that since the formation, the heat distribution has not changed very much due to the thermal conduction. However, radioactive decay would add another component to the heat profile in a manner depending on the largely unknown distribution of uranium, thorium, and potassium. Hence, it is possible that also the central part of the Moon, although accumulated cold, is now partially melted, as suggested by seismic evidence (Latham et al., 1973).

9. A Simple Model for Accumulation of Water

The rate of increase of mass with radius of an embryo of uniform density is

$$\frac{dM_e}{dR} = 4\pi R^2 \theta \quad (14)$$

Let us suppose that each mass unit of impacting matter releases ϵ mass units of water. Then the rate of increase of water content in the environment of the embryo is

$$\frac{dM_{H_2O}}{dR} = \epsilon \frac{dM_e}{dR} = \epsilon 4\pi R^2 \theta \quad (15)$$

The water vapor in the upper atmosphere will approach an equilibrium temperature T and a corresponding Maxwellian velocity distribution. The molecules that have thermal velocity v in excess of the escape velocity v_e for the embryo can escape immediately from the neighborhood of the embryo. As shown by Jeans, if the root mean square velocity of a gas is only of the order of 20% of the escape velocity, the gas can escape entirely in the course of a billion years or so. Let us make a conservative estimate of the retention of water molecules and assume that all molecules having velocities higher than $0.2 v_e$ will escape from the gravitational field of an embryo.

Hence, we have to multiply the right-hand side of equation 15 by the fraction representing the number of molecules that are retained:

$$\frac{dM_{H_2O}}{dR} = \epsilon 4\pi R^2 \theta \frac{4}{\sqrt{\pi}} \int_0^{X(R)} e^{-x^2} x^2 dx \quad (16)$$

with

$$x = v \left(\frac{m_{H_2O}}{2kT} \right)^{1/2}$$

$$X(R) = 0.2v_e \left(\frac{m_{H_2O}}{2kT} \right)^{1/2} = 0.2 \left(\frac{8}{3} \pi k \theta \right)^{1/2} R \left(\frac{m_{H_2O}}{2kT} \right)^{1/2}$$

where m_{H_2O} and k are the mass of a water molecule and the Boltzmann constant, respectively. Therefore, the total mass of water that has accumulated when the embryo had a radius R is

$$M_{H_2O}(R) = \epsilon 16\pi^{1/2} \theta \int_0^R R^2 \left[\int_0^{X(R)} e^{-x^2} x^2 dx \right] dR \quad (17)$$

Is the accumulation of water described by equation 17 up to the time when the planet has attained its final size sufficient to account for the ocean mass? In order to answer this question, we need to specify the value of the parameter ϵ . Instead, we shall turn the question around and ask what value of ϵ will give a total accumulation equal to the present ocean mass; we can then examine the implications of this value of ϵ .

The relevant temperature T of the water vapor that will determine its rate of gravitational escape is a characteristic temperature at the top of the atmosphere that forms by the release of the occluded gases. This temperature is not related to the accretionally heated surface temperature of the embryo, but is determined by the radiation fields of the Sun and of the plasma in the primordial magnetosphere surrounding the Earth (De and Arrhenius, 1973). Assuming that the thermal conditions at the top of the atmosphere were comparable to those in the Earth's exosphere today, we choose a characteristic temperature of 1000°K. Our analysis does not change appreciably if T is lower than 1000°K. If T were as high as 3000°K, this would lower the total accumulation of water by about a factor of 2.

For the density θ , we adopt for convenience the average density 5.5 g/cm³ of Earth. It is possible that the Earth formed from relatively homogeneous material of lower density. The high-density core would in this case be produced by a phase transformation setting in when the Earth had reached about 0.8 of its present radius (Lodochnikov, 1939; Ramsey, 1948, 1949, 1967; see also discussion in Levin, 1972 and Alfvén and Arrhenius, 1973b). The original density of this material is then likely to be of the order of 3 to 4 g/cm³—but as far as the present analysis is concerned, the assumption of average density is not critical.

Figure 3 shows the accumulation of water with increasing radius of the protoplanet calculated on the basis of equation 17. The total accumulation when the radius reaches the present value has been matched to equal the present ocean mass. The value of ϵ needed for this is $\epsilon \approx 3.2 \times 10^{-4}$.

Meteorite materials of the type discussed in Section 4 have values of ϵ in the range 10^{-2} to 10^{-3} , hence primordial grains in principle would satisfy the required value for ϵ . Figure 3 also shows the primeval heat structure of the Earth resulting from accretion, as discussed in Section 8. The ordinate (left) for this curve is given in arbitrary

units and is proportional to the temperature. We note that after the low temperature accretion of the inner core, the temperature of the surface layer of the embryonic Earth continues to rise and culminates at $R \approx 0.4R_{\oplus}$. Hence water vapor cannot condense during this period and must remain in the atmosphere. However, the gravitational retention of water vapor at this stage is very small. As the accretion proceeds, now at a low rate determined by the injection of source gas into the terrestrial region, the surface temperature of the protoplanet falls to a low average value that is probably close to the present surface temperature of the Earth. This would allow the water vapor to condense and begin the formation of a proto-ocean.

10. Accretional Heat Front and State of Water

As shown in Section 8 and Fig. 3 for the case of the Earth, heat delivery to the surface layer of the protoplanet first reached a maximum and then declined to a low mean value when the size of the present outer core was reached. After this culmination, the accretion of the outer regions of the Earth proceeded at a low rate, controlled by the continued injection rate of matter (assumed here to be constant) into the terrestrial region of space and terminating at the time τ_i when this injection ceased. During the era preceding τ_i , the average rate of heating of the surface protoplanet hence must have been low. At the same time, however, the local heating at each individual impact site continued to be high and actually increased as a function of R as the escape velocity of the Earth increased due to its increasing mass. The transformation of kinetic energy of the infalling bodies to thermal energy has been discussed in Section 7. Since the major fraction of mass, and hence potential thermal energy, is concentrated in the largest embryos impacting on the growing Earth (Gurevich and Lebedinskij, 1950), it is these large projectiles that control the thermal evolution.

Assuming that the size distribution of accreting planetesimals was such as to place the major fraction of mass in bodies sufficiently large to penetrate the atmosphere and the ocean, the major fraction of heat was delivered in large impacts repeated relatively rarely at any given location (once every 10 to a few hundred years in any impact area) during the era of mantle and crust formation. Each major impact is likely to have created a deep subsurface region of molten rock that, in contrast to secondary ejecta and a thin surface crust, would cool slowly. In such melt reservoirs differentiation of magma could take place with the heavy components sinking to the bottom and the light materials accumulating at the top. Although the average surface temperature of the Earth during this era would have remained low, each individual impact region would, in the course of time, be remelted and differentiated many times over. Radial progression of this accretional heat front, discontinuous in space and time, resulted in the selective removal toward the surface of light differentiates forming the Earth's crust, and of volatiles forming the atmosphere and the ocean.

The water vapor released at individual impacts would, after time τ_c , condense and contribute to the growing proto-ocean due to the low average surface temperature during this era.

11. Details of Model

The development discussed in Sections 8 and 9 has purposely been made simplistic in order to illustrate in principle the energetics of growth of the planet and the course of retention of oceanic and atmospheric components with time. There are several complicating factors, some of which can be discussed qualitatively with some assur-

ance at the present time; for others, observational basis is still lacking. Some of the resulting modifications and uncertainties are discussed in the following sections.

A. Atmospheric Loss Mechanism

In the calculation in Section 9, it was assumed that water vapor is lost from the exosphere by molecular evaporation. If one assumes solar energy flux of at least the present magnitude, water vapor in the upper atmosphere will be dissociated and form a number of species, including atomic and molecular hydrogen, hydroxyl and oxygen ions; of these, the hydrogen species have a high escape rate and are preferentially lost to space. The escape rate is probably controlled by the transfer rate of water vapor from the troposphere across the stratospheric cold trap (Harteck and Jensen, 1948; Urey, 1952, 1959).

It is thus generally believed that a part of the terrestrial oxygen is the residue of water from which the hydrogen component has escaped. An estimate of the relative importance of this selective loss can be obtained from the budget shown in Table I.

TABLE I

Oxygen Reservoirs	Mass of Stored Oxygen (10^{23} g)
Hydrosphere (including sediment porewater)	16.7
Limestone	4
Excess in oxidized iron compounds	0.2
Atmosphere	0.05
Sulfates	0.04

The table shows that if we make the extreme assumption that the oxygen now present in carbonates derives entirely from dissociated water by reaction of such oxygen with primordial carbon compounds, then limestone would be a major store of such oxygen. However, the carbonates may partly or entirely have formed by other reactions instead; carbon dioxide may have been a primordial gas component of planetesimals (Gibson and Moore, 1973a), it may have been produced by reaction of planetesimal carbon with oxygen in iron silicate in the accretional heat front (Ringwood, 1959), or carbonates could have formed by reaction of methane and water with silicates (Urey, 1952). Hence the largest conceivable loss of water by escape of hydrogen would amount to about 25% of the present mass of water; the actual amount is probably much smaller.

The amount of atmospheric oxygen used up by oxidation of transition element compounds, primarily those of iron, has been estimated on the basis of the extreme assumption of an original oxygen-iron average oxidation state corresponding to FeO ; furthermore all iron in present-day sediments occurs as Fe_2O_3 and forms on the average 3.5% of shale and deep-sea sediments. The total thus obtained is only a small fraction of the oxygen in the present ocean. However, this calculation ignores the unknown amount of water-derived oxygen bound to divalent or trivalent iron in the mantle and in crustal igneous rocks (see Holland, 1964). Particularly the amount in the mantle constitutes a substantial uncertainty.

The rate of removal of gas from bodies in space is also affected by interaction with corpuscular radiation from the Sun. It is sometimes assumed that a "solar gale" arose

after the planets had formed, removing all planetary atmospheres in the inner part of the solar system.

The need for such an *ad hoc* mechanism was rooted in the belief that the primordial components were missing from the Earth's atmosphere. As discussed in Section 4, it is now realized that on the contrary, our present atmosphere can only be understood as a product of the primordial accumulation, modified by loss of hydrogen and helium, by photochemical and biological processes, and by reaction with the solid Earth, from which radiogenic gases have also been added. The records from the Moon and from meteorites also have failed to give evidence of any major enhancement of solar corpuscular radiation after the formative era. For a discussion of the corpuscular radiation effects during this era, see Alfvén and Arrhenius, 1973, Section 11.8.

B. Effect of Atmosphere and Ocean on Accretional Heating

The developing hydrosphere and atmosphere could, in principle, introduce effects on the distribution of heat received in the accretional process. This is partly because some of the projectile energy will be dissipated by frictional heating of the atmosphere and the ocean and partly because these will decrease the efficiency of cooling by reradiation into space from collision-heated spots on the surface. The latter effect would become important if a large fraction of accumulated water were evaporated into a hot atmosphere. This is, however, not likely to have taken place since such a runaway greenhouse effect (Rasool and de Bergh, 1970) would probably be irreversible, whereas the geological record shows existence of sediments and organic life on Earth already at the -3 Gy level (Engel et al., 1968). The lack of development of a hot atmosphere can be understood, since the calculated size distribution of accumulating planetesimals place the major amount of mass in large projectiles (Section 10). This would concentrate the accretional heat to limited regions, and with sufficient intervening time available for efficient reradiation of surficial heat into space.

At a large projectile mass-surface ratio, the energy dissipation in the atmosphere and the ocean would also become small compared to the energy release after penetration to the solid surface (Lin, 1966). Terrestrial experience gives no guidance concerning the nature of impact processes of the magnitude involved here. Until these effects could be studied directly in the preserved impact record of the Moon, it would be difficult to predict the relative distribution of projectile matter between ejecta dissipating energy over wide regions, and the retained projectile fraction implanted in the target and melting itself as well as the target material. In the projectile mass range covered by controlled experiments, the mass of ejecta exceeds that of the projectile in hypersonic impacts (Gault et al., 1968; Neukum et al., 1970). At projectile masses far beyond this range, however, the fraction of projectile material retained in the target would be expected to increase, particularly at impact speeds several times the sound velocity in the projectile material. This is indicated by the effects of the largest impacts on the lunar surface. Hence local implantation of kinetic energy converted to heat is likely to have been an important process at the accretion of the Earth.

12. Volatiles in the Lithosphere

Crustal igneous rocks on Earth have a low but persistent content of water and occasionally very high contents of carbon dioxide (von Eckermann, 1948, 1958; Tuttle and Gittens, 1966). Because of the unknown extent of these components with depth in the Earth, the total store of volatiles in the solid Earth is highly uncertain.

The question how and when these volatiles became buried is important to the problem of the formation of the ocean. One suggestion has been that an excess over the present amount was introduced into the interior of the Earth during its early history. This situation would be or would become metastable, causing a net transport of water from the lithosphere to add to the volume of the ocean during a substantial fraction of geological time and possibly still today. No observational basis seems to exist for this assumption, which was originally made to secure a storage place for the present ocean and atmosphere while the original atmosphere was supposed to be destroyed. As discussed above, such a catastrophe is counterindicated by the noble gas distribution in the atmosphere, hence the need for temporary ocean storage has disappeared.

To explain the present content of reactive volatiles (primarily water and carbon dioxide) in igneous rocks, Fanale (1971), on the basis of a proposal that the Earth became completely melted (Hanks and Anderson, 1969), suggested that the volatiles were partitioned in equilibrium between the melted Earth and a hot atmosphere in contact with it. This would seem excluded on the basis of quantitative considerations of the accumulation process (Safronov, 1954, 1958, 1959, 1960, 1969; Alfvén and Arrhenius, 1970a, b; Section 6 in this chapter). These indicate early exhaustion of the Earth's jet stream, and slow subsequent growth during the major part of the approximately 10^8 -yr accretion period. If this is correct, the average temperature of the Earth's surface must have been low during accumulation of the mantle and the crust. The thorough outgassing of the noble gases recognized by Fanale is, as demonstrated by the late bombardment effects on the Moon, the natural consequence of the local heating at each individual impact and does not in itself require simultaneous heating of the whole Earth. It is furthermore doubtful that a thoroughly melted Earth would have had time to cool to yield a still-preserved crust 0.7 Gy after formation, particularly with a hot atmosphere containing a major part of the present ocean and of the carbon dioxide reservoir. Finally, the spotty occurrence of deep-seated igneous rocks rich in carbon dioxide suggests that it was introduced locally by a mechanism such as described below, rather than by equilibration of a molten Earth with a hot, massive atmosphere.

There is indeed a straightforward and observationally supported way in which the igneous rocks of the crust and upper mantle would seem to be continuously impregnated with reactive volatiles from the atmosphere and the ocean. The evidence for convection-driven lateral movement of large plates of the Earth's crust suggests strongly that water and carbonate-containing sediments and hydrated submarine eruptives are sinking and assimilating into the upper mantle in subduction zones, compensating for the rise of magma and generation of new crust in the sea floor spreading zones. This vertical mixing is sufficiently fast (approximately 5 cm/yr) to have drowned all ocean sediments appreciably older than a few per cent of the estimated age of the Earth. Hence all reactive volatiles now found in igneous rocks can be understood as contamination mainly from the ocean, introduced into the solid Earth much later than the time of formation of the primordial crust. A potential measure of the efficiency of this cycling is the remaining effusion from the Earth's interior of stable end products from such radioactive species that decayed practically completely a short time after the formation of the Earth (Xe^{129} from I^{129} , half-life approximately 15 My; see Boulou and Manuel, 1971). Another suggested indicator would be He^3 , possibly inherited as a cosmic ray spallation product from primordial material (Clarke et al., 1969). It would, however, seem difficult to understand how helium could survive accretional degassing while neon, argon and krypton were transferred to the primordial atmosphere with such efficiency that no traces have been found of their primordial component in terrestrial igneous rocks.

It should be clear from this discussion that an efficient mechanism for circulation of volatiles between the ocean-atmospheric system and the upper mantle has been operating through the geological eras recorded on the ocean floor and presumably during the entire history of the Earth after its formation. This does not exclude the possibility that a fraction of the primordial volatiles were left behind in the growing lithosphere as a result of incomplete outgassing at accumulation of the Earth.

At atmospheric pressure the equilibrium solubilities in silicate melts of most gases are modest. However, considerable excess amounts of gas can be incorporated, at the moment of shock, in melted, gas-rich materials and can be retained in disequilibrium in such melts when they solidify due to the inefficiency of diffusion-limited removal processes. On the other hand, convection in such melts, and stripping by boiling of components such as hydrocarbons and monoxides of carbon, silicon, and potassium, contribute toward relieving such disequilibria. These retention and removal phenomena are exemplified in the lunar rocks. Conditions in the lunar crust also indicate that in the culminating stage of accretional heating (which on Earth probably occurred at the outer core and on the Moon not far below the present surface), the removal of any water vapor possibly associated with the molten and vaporized projectile material was highly efficient, resulting in oxygen partial pressure less than 10^{-14} b. The sporadic occurrences of volatiles in lunar materials are considered to derive from post-formative impact of volatile-rich projectiles on the cold lunar surface and in some instances perhaps to be due to vapor transport through crustal fractures from the coldly accreted inner core (which could be considerably warmer today due to radioactive heating).

During the accretion of the Earth's mantle and crust, the large impacts could well have implanted hydroxyl-containing material sufficiently deep so that the solubility in the melt remained comparatively high, and removal was not complete before solidification in spite of repeated remelting by new impacts and gravitational upward removal of light components resulting in formation of the crust. Because of the complexity of these processes and our lack of knowledge of large-scale impact effects, it is difficult now to estimate the ultimate efficiency of the materials separation by the accretional heat front.

A continued systematic search for primordial gas components in the effluents from the Earth's crust and mantle could narrow the limits of uncertainty. Improved knowledge of the temperature distribution in the mantle would also contribute to the vertical transport efficiency problem, since at least at moderate pressures the large cations of the elements contributing to radioactive heating are concentrated in the light component migrating toward the surface in the accretional heat front.

13. The Ocean and the Earth-Moon System

It is likely that the evolution of the ocean has been markedly affected by the fact that an abnormally massive body causing significant tidal effects exists in the vicinity of the Earth. A similar case is that of Neptune with the captured satellite Triton, which has a tidally modified orbit (McCord, 1966).

After the recent exploration of the Moon, two types of theories for its origin remain to be discussed. One postulates the formation of the Moon in an independent solar orbit (Gerstenkorn, 1969) or coupled by resonance to the Earth (Alfvén and Arrhenius, 1969, 1972) and in either case subsequently captured by tidal interaction. The other (Ringwood, 1970) proposes that the Moon formed around the Earth by hydromagnetic transfer of angular momentum to a primordial plasma emplaced around the planet in

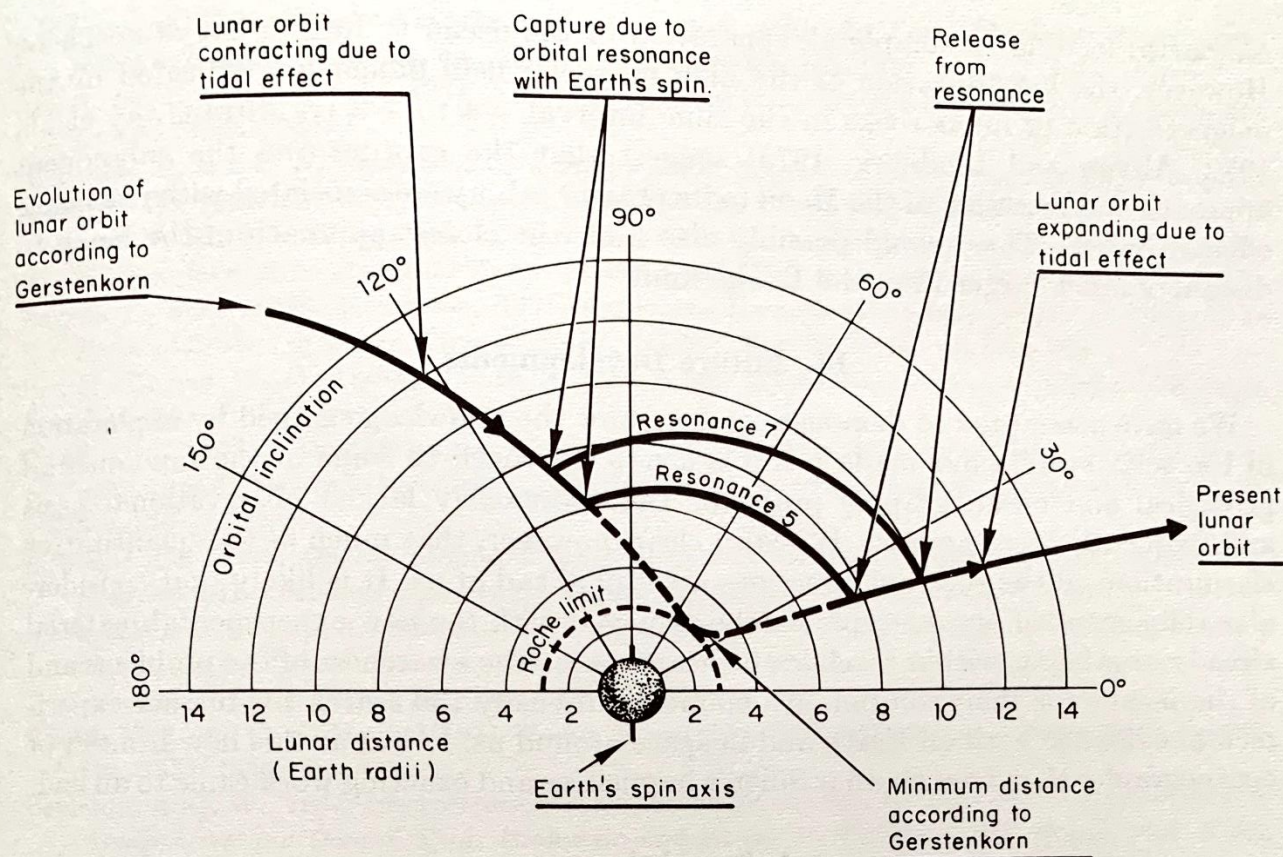


Fig. 4. Noncatastrophic capture: spin-orbit resonance prevents the Moon from reaching the Roche limit. The retrograde lunar capture orbit contracts due to tidal dissipation, until resonance between the lunar orbit period and the spin period of the Earth locks the Moon in a slowly expanding orbit. Since the Moon never comes very close, no breakup or autoejection occurs and the tides do not reach catastrophic heights. When the orbital inclination has decreased below a critical angle (suggested in the diagram at about 25°), the resonance locking is broken and the Moon recedes to its present orbit at 60 $R_{\oplus}$. From Alfvén and Arrhenius (1969).

the same way as the (structurally very different) regular satellite systems seem to have formed.

The former hypothesis would appear more likely in view of the fact that the Moon is much more massive (mass ratio 1:80 relative to Earth) than the regular satellites of Jupiter, Uranus, and Saturn where the ratios of satellite mass to central body are less than 1:10⁴.

A comparison of Earth with the regular planet-satellite systems of Jupiter, Saturn, and Uranus (Alfvén and Arrhenius, 1972, Fig. 1) suggests that the Earth indeed may have had a regular satellite system, composed of about half a dozen bodies, each with a mass of only a fraction of a percent of the lunar mass. These proper satellites could have been swept up by the Moon during the postcapture evolution of its orbit; the major maria may be the impact sites, and the active time interval -4.0 to -3.0 Gy would mark this series of events.

Regardless of the ultimate origin of the Moon, tidal forces in the early evolution of the Earth-Moon system should be of considerable importance, and the question arises of the relative role of the ocean in the tidal dissipation. Since dissipation in the solid Earth is considered insignificant (Munk, 1968), the ocean would provide the most important medium for tidal energy exchange.

It was believed earlier that capture of the Moon must have catastrophic tidal effects

on Earth, leading to complete evaporation of the ocean to form a hot atmosphere. However, the long duration of the high magnetic field immersion indicated by the magnetization of lunar rocks in the time interval -4 to -3 Gy (Strangway et al., 1972; Alfvén and Lindberg, 1973) suggest that the capture and the subsequent approach and recession of the Moon to its present orbit were associated with resonance effects (Fig. 4). These could possibly also limit the closest approach of the Moon to distances much larger than the Roche limit.

14. Future Developments

We have attempted to demonstrate here how the knowledge gained by exploration of the solar system has made possible a new approach to some of the fundamental geological and oceanographic problems that previously lacked observational basis and frequently were ignored. It is also clear, however, that much of the quantitative clarifications of the relevant processes are still ahead of us. It is likely that considerable refinement of our concepts can be achieved with the new experimental material already existing or within reach in the near future. The awareness of the problems and of the means for their solution are bound to intensify the search for further experimental evidence both on Earth and in space around us. It was at this new frontier of oceanography that Lars Gunnar Sillén's inquisitive and exacting work came to an end.

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